PATENT ABSTRACTS OF JAPAN

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(54) ITO SINTERED COMPACT AND SPUTTERING TARGET

(57)Abstract:
PURPOSE: To obtain a sputtering target excellent in productivity at a high density and at a high film forming rate by incorporating Zn, Cu, Sb, Ti, Tm, Li and Mg into an ITO sintered compact constituted of indium oxide and tin oxide.
CONSTITUTION: An ITO sintered body constituted of indium oxide and tin oxide is incorporated with about 5-5000ppm of one or more kinds of elements among Zn, Cu, Sb, Ti, Tm, Li and Mg, and its density is regulated to 90-100%. The content of tin oxide in the sintered body is preferably regulated to about 1-20wt.%. This sintered body is obtd. by mixing and compacting the raw material powder in a specific ratio, subjecting the green compact to cold hydrostatic pressing and thereafter executing sintering at about 1250-1600°C. By executing sputtering with the ITO sintered body as a target, the ITO film having low resistance and excellent in electrical conductivity and light transmissivity in spite of the substrate temp. is obtained at a high film forming rate, and the occurrence of surface cracking, nodules, the scattering of broken fine materials or the like in the target can be prevented.

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ITO +Ti 001

ρ 5×10⁻⁵ 003

Ti : Table 2

300°, 1%O₂ Table 3

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The ITO sintered compact of 90% - 100% of consistencies characterized by containing one or more sorts of elements chosen from zinc, copper, antimony, titanium, a thulium, a lithium, and magnesium in the ITO sintered compact which consists of indium oxide and tin oxide.
[Claim 2] The sputtering target which consists of an ITO sintered compact of a publication of claim 1 term.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the ITO sintered compact which was excellent as a sputtering target.
[0002]
[Description of the Prior Art] While the need of the transparence electric conduction film is increasing with development of the display device centering on liquid crystal, the ITO (indium oxide, tin oxide) film is widely used in respect of low resistance and high transparency in the transparence electric conduction film. As the formation approach of the ITO transparence electric conduction film, the point of the simplicity of operability to the sputtering method is common, and the sputtering method using the target which consists of an ITO sintered compact is applied widely. Recently requires the highly efficient ITO transparence electric conduction film especially with adoption of colorization of liquid crystal, detailed-izing of a component, and an active-matrix method.
[0003] Usually, an ITO sintered compact sinters the mixed powder (ITO powder) of indium oxide powder and tin oxide powder after pressurization molding, and is manufactured.
[0004] Preparation of the indium oxide powder used as a raw material of an ITO sintered compact, or tin oxide powder As an approach of pyrolyzing each metal hydroxide, an organic metal salt, an inorganic metal salt, a sol, gel, etc., and preparing direct ITO powder The product which adds and carried out coprecipitation of the precipitate formation agent to the homogeneity mixed solution of an indium and tin (For example, JP,62-7627,A, JP,60-186416,A, etc.) The method of decomposing thermally and manufacturing the products (for example, JP,58-36925,A etc.) generated by hydrolysis etc. is learned.
[0005] However, the consistency of the sintered compact obtained from the raw material powder obtained by such approach could not have still sufficient consistency, but was what is about 65% of 7.15 g/cm3 which is the theoretical density of an ITO sintered compact (10% content of tin oxide) (- 4.65 g/cm3). The ITO sintered compact with such a low consistency had the trouble that spatter operability -- generating of the nodule by

reduction of about [that the membrane formation of the highly efficient ITO film excellent in conductivity and light transmission nature was very difficult] and a target front face and a membrane formation rate are slow -- was bad, when it was bad, and conductivity used this as a sputtering target, since thermal conductivity and anti-**** were low.

[0006] In order to solve such a problem, the method of obtaining a high-density ITO sintered compact is examined variously, and the approach of adding Si, germanium, etc. as sintering acid to an ITO sintered compact is proposed as the example (for example, JP,61-136954,A).

[0007] however -- the inside of the transparence electric conduction film obtained from the spatter phosphorus GUTAHE get which needs to make [many] the addition of Si, germanium, etc. and consists of such a sintered compact in order to obtain a high-density sintered compact -- Si and germanium -- mixing -- low -- it was difficult to obtain the film [****].

[0008]

[Problem(s) to be Solved by the Invention] Therefore, the ITO film excellent in conductivity and light transmission nature could be given, and an ITO sintered compact without the problem on which generating of the nodule by reduction of a target front face, the crack of a target, and the breakage particle object from a target scatter was desired.

[0009]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for the ability of the sintered compact containing one or more sorts of elements chosen from zinc, copper, antimony, titanium, a thulium, a lithium, and magnesium to attain high sintered density in the sintered compact which consists of indium oxide and tin oxide, as a result of repeating examination wholeheartedly in view of the above present condition.

[0010] Hereafter, this invention is explained to a detail.

[0011] The ITO sintered compact of this invention contains one or more sorts of elements chosen from zinc, copper, antimony, titanium, a thulium, a lithium, and magnesium. As a content of these elements, the 5-5000 ppm of the 10-500 ppm of the total contents are 20-200 ppm especially preferably preferably to the sintered compact whole quantity. Less than 5 ppm of an addition are [the effectiveness] insufficient, and on the other hand, even if it surpasses and adds 5000 ppm, the effectiveness of the improvement in sintered density is saturated, and it is not economical.

[0012] The content of the tin in the ITO sintered compact in this invention is 2 - 15 % of the weight especially preferably one to 20% of the weight in tin oxide conversion.

[0013] Especially the specific resistance of the film with which the consistency of the ITO sintered compact of this invention was obtained 90% to 100% of true density, using this ITO sintered compact as a sputtering target serves as 5x10-5 - 7x10-4ohmcm below 1x10-3ohmcm. such -- low -- it is because that the film [****] is obtained has low resistance of a sintered compact, so the damage to the film by the anion which there is little power consumption, and discharge of it is attained on a low electrical potential difference, and is generated in the plasma decreases.

[0014] Moreover, sintering particle size is 1-20 micrometers, and the ITO sintered compact of this invention is 2-20 micrometers especially. The sintering particle size of the conventional ITO sintered compact is 30 micrometers or more in a hotpress at less than 1 micrometer and pressurization-among oxygen elevated-temperature sintering. In a less than 1-micrometer small sintered compact, a membrane formation rate has a late sintering particle size, and since sintered compact reinforcement is weak, it has the problem that it is divided during a spatter, or a sintered compact is missing, and a granular object scatters on the film. On the other hand, since the sintered compact which has sintering particle size [good] for 20 micrometers has small shock resistance, it is easy to be divided, and since the coefficient of thermal expansion is still larger, from a bonding side, it exfoliates or is easy to be divided during a spatter. Next, the example is illustrated about the manufacture approach of the sintered compact of this invention.
[0015] The ITO sintered compact of this invention can be manufactured by mixing, casting and sintering the compound of one or more sorts of elements chosen from indium oxide, tin oxide, zinc and copper, antimony, titanium, a thulium, a lithium, and magnesium, for example, an oxide, a salt, etc. What is necessary is just to heat-treat especially the mixed approach of the compound containing indium oxide, tin oxide, and the above-mentioned element after mixing indium oxide, tin oxide, and this compound, for example, although not limited. In addition, this invention does not remove the case where one or more sorts of elements chosen from zinc, copper, antimony, titanium, a thulium, a lithium, and magnesium into indium oxide and/or tin oxide are contained as an impurity.
[0016] As other approaches, after obtaining the precursor of an indium and/or tin, and this compound with a coprecipitation method etc., the approach of heat-treating can be illustrated.
[0017] Although the mixed state or an integrated state is sufficient as one or more sorts of elements chosen from indium oxide, tin oxide, zinc and copper, antimony, titanium, a thulium, a lithium, and magnesium, as for especially zinc, copper, and antimony, it is desirable that they are tin oxide and an integrated state, and, as for titanium, a thulium, a lithium, and magnesium, it is desirable that they are indium oxide and an integrated state. With an integrated state, it is attained by being able to illustrate for example, a dissolution condition etc., for example, heat-treating the compound of indium oxide and/or tin oxide, and these elements at 600 degrees C - 1800 degrees C.
[0018] That is, it is desirable to mix them with indium oxide in this invention, after zinc, copper, and antimony make tin oxide dissolve, for being referred to as ITO to be desirable, they to be mixed with tin oxide after titanium, a thulium, a lithium, and magnesium make indium oxide dissolve, and to be referred to as ITO.
[0019] The amount of dissolution of these elements to indium oxide and tin oxide is adjusted so that the content in the ITO sintered compact finally obtained may become 5-5000 ppm of **.
[0020] Although especially the indium oxide to be used is not limited, it is desirable that it is detailed and uniform indium oxide excellent in the degree of sintering. For example, as for the BET surface area of indium oxide powder, it is desirable that it is more than

10m2/g.
[0021] As for the tin oxide used on the other hand, it is desirable that surface area is small, and it is desirable that BET surface area is below 1m2/g especially below 3m2/g.
[0022] Especially the mixed approach of the compound which consists of one or more sorts of elements chosen from indium oxide powder, tin oxide powder and zinc, copper, antimony, titanium, a thulium, a lithium, and magnesium is not limited, but wet [, such as a ball mill using balls, such as a zirconia and urethane resin, a vibration mill or a V type blender and a stone milling machine,] or a dry-type mixed approach is illustrated.
[0023] Next, it is not limited especially although the metal mold casting method, the cast casting method, etc. are mentioned that what is necessary is just to choose the molding approach whose target configuration the molding approach suited although powder is cast.
[0024] As for a molding object, because of the densification of a sintered compact, it is desirable to carry out pressure treatment in a cold isostatic press. The pressure at that time may be good at about two 3 - 5 t/cm, and may repeat processing 2 to 5 times if needed.
[0025] 1250-1600 degrees C of acquired molding objects are especially sintered at the temperature of 1350-1500 degrees C preferably. When less than 90% of ITO sintered compact is obtained for a consistency when sintering temperature is less than 1250 degrees C, and sintering temperature exceeds 1600 degrees C, unusual growth of a sintered compact particle may arise. Especially sintering time amount is enough in [from 10 hours] 30 hours for several hours to dozens hours. What is necessary is not to limit especially a sintered atmosphere but just to perform it by the inert gas middle class among atmospheric air and oxygen.
[0026]
[Effect of the Invention] So that clearly from the above explanation The zinc of this invention, copper, antimony, titanium, The sputtering target which consists of an ITO sintered compact containing one or more sorts of elements chosen from a thulium, a lithium, and magnesium The transparent transparence electric conduction film is given. the low-temperature substrate which is not heated in the heated elevated-temperature substrate -- also setting -- very -- low resistance -- quantity -- in addition -- and the membrane formation rate -- quick -- the granular product on the front face of a target -- there is nothing -- the crack of a target, and the breakage particle from a target -- also scattering -- there is nothing and it excels in productivity extremely.
[0027]
[Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to this.
[0028] The tin oxide of example 1BET surface area of 1m 2/g and the oxide of each element of zinc, copper, and antimony were heated in atmospheric air after mixing, respectively, and these elements were made to dissolve to tin oxide. After mixing further the tin oxide and indium oxide containing these elements and carrying out the die press of the obtained mixed powder, hydrostatic-pressure press processing was carried out by 3 ton/cm2, it sintered at 1500 degrees C among oxygen for 24 hours, and the ITO sintered compact was obtained (indium oxide/tin oxide = about 90/10 (weight ratio), sintering

particle-size =9micrometer). In addition, it was made for the content of each element in the ITO sintered compact whose addition of zinc, copper, and antimony is an end product to be set to 50 ppm, 100 ppm, and 500 ppm. The physical properties of these sintered compacts are shown in Table 1.

[0029] Then, the spatter conditions shown in Table 3 show to Table 1 in accordance with the result which carried out sputtering membrane formation, using the obtained sintered compact as a target.

[0030] The indium oxide of example 2BET surface area of 20m 2/g and the oxide of each element of titanium, a thulium, a lithium, and magnesium were heated in atmospheric air after mixing, respectively, and these elements of indium oxide were made to dissolve. After mixing further the indium oxide and tin oxide containing these elements and carrying out the die press of the obtained mixed powder, hydrostatic-pressure press processing was carried out by 3 ton/cm2, it sintered at 1500 degrees C among oxygen for 24 hours, and the ITO sintered compact was obtained (indium oxide/tin oxide = about 90/10 (weight ratio), sintering particle-size =8micrometer). In addition, the addition of each element was set up like the example 1. The physical properties of these sintered compacts are shown in Table 2.

[0031] Then, the same spatter conditions as an example 1 show to Table 2 in accordance with the result which carried out sputtering membrane formation, using the obtained sintered compact as a target.

[0032] After mixing the indium oxide of example BET surface area of comparison of 20m 2/g, and the tin oxide of BET surface area of 1m 2/g and carrying out the die press of the obtained mixed powder, hydrostatic-pressure press processing was carried out by 3 ton/cm2, it sintered at 1500 degrees C among oxygen for 24 hours, and the ITO sintered compact was obtained. (indium oxide/tin oxide = about 90/10 (weight ratio), sintering particle-size =7micrometer) . These physical properties are shown in Table 2.

[0033] Then, the same spatter conditions as an example 1 show to Table 2 in accordance with the result which carried out sputtering membrane formation, using the obtained sintered compact as a target.

[0034]

[Table 1]

	添加元素	添加量 (ppm)	固溶温度 (℃)	密度 (%)	焼結体比抵抗[1)]	透明導電膜比抵抗[1)]		
						100℃	200℃	300℃
実施例1	Zn	50	1500	94.1	2.5	2.8	2.1	1.5
		100	1500	96.3	2.4	2.9	2.1	1.6
		500	1500	97.2	2.5	2.9	2.2	1.5
	Cu	50	1500	94.4	2.4	2.9	2.2	1.6
		100	1500	96.5	2.8	2.9	2.3	1.7
		500	1500	98.2	2.4	3.0	2.2	1.8
	Sb	50	1500	94.7	2.3	2.7	2.1	1.9
		100	1500	95.8	2.6	2.8	2.2	1.8
		500	1500	95.2	2.5	2.8	2.1	1.8

1) 単位 : $\times 10^{-4}\Omega cm$

[0035]
[Table 2]

	添加元素	添加量 (ppm)	固溶温度 (℃)	密度 (%)	焼結体比抵抗[1)]	透明導電膜比抵抗[1)]		
						100℃	200℃	300℃
実施例2	Ti	50	750	94.6	2.8	2.9	2.2	1.7
		100	750	94.2	2.7	2.8	2.1	1.7
		500	750	95.9	2.5	2.8	2.4	1.8
	Tm	50	750	94.8	2.6	2.9	2.1	1.6
		100	750	95.3	2.7	2.9	2.2	1.7
		500	750	95.6	2.5	3.1	2.2	1.7
	Li	50	750	94.8	2.4	2.8	2.3	1.9
		100	750	96.2	2.5	2.9	2.2	1.7
		500	750	97.2	2.7	2.8	2.2	1.8
	Mg	50	750	93.8	2.4	2.8	2.3	1.9
		100	750	93.9	2.5	2.7	2.2	1.8
		500	750	94.8	2.8	2.8	2.3	1.7
比較例		-	-	88.0	3.0	3.5	2.4	1.9

1) 単位 : $\times 10^{-4}\Omega cm$

[0036]
[Table 3]

スパッタ方式	ＤＣマグネトロンスパッタ
ターゲット	直径３インチφ
基板	コーニング＃７０５９ガラス
基板温度	１００℃，２００℃，３００℃
ターゲット－基板間距離	４５ｍｍ
ガス	酸素１％含有アルゴン
ガス圧	０．５Ｐａ
投入電力	３Ｗ／ｃｍ^2
膜厚	３０００オングストローム

[Translation done.]